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ION-DIPOLE COLLISIONS: "CLASSICAL TUNNELING"

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ABSTRACT

Numerical studies of ion-dipole collisions are extended to calculating the effects of vibrational degrees of freedom on capture cross sections and formation of ion-molecule complexes. Two different dipole moment variations about the equilibrium internuclear separation of the oscillator are studied. The capture cross section is sensitive to the oscillator model. Computer-made motion pictures reveal a change in mode of the oscillation due to the ion-dipole interaction. The oscillator becomes constrained so it cannot relax to its equilibrium separation. This shift in oscillator potential barrier is denoted as "classical tunneling" of the oscillator.

INTRODUCTION

Capture cross sections and collision complex lifetimes have been cal-
culated numerically for ion-polar molecule collisions.[1-5] The energy

transfer in these collisions has been studied using computer-plotter tech-
niques.[4-5] (The polar target molecule is represented by a rotating dipole

imbedded in a polarizable sphere. The ion is made to reflect at an inter-

molecular distance r_c to simulate the hard repulsive cores of the ion

and molecule.) Capture cross sections have been calculated to set an up-

per limit to ion-molecule reaction cross sections and to compare the pre-

dicted ion energy dependence with mass spectrometric results.[6-8] The

permanent dipole introduces multiple reflection behavior[3] corresponding to

the formation of long-lived ion-molecule collision complexes. These com-

plexes may be of importance as clustering sites in gas discharges or ir-

radiated gases. (Such "captures" have calculated collision lifetimes as

large as several hundred times a single reflection period.) Motion pic-

tures have also been made with the computer to study hindered rotation of

the dipole by the incident ion.[5] Hindering may favor a specific chemical

reaction.

Lifetimes for multiple-reflection collisions have previously been

calculated including rotational and translational degrees of freedom for

the ion-molecule collision pair. This paper reports on numerical studies

of vibrational effects on the capture cross section, the probability of

multiple reflections, and collision lifetimes. The vibrational effects

are included by approximating the polar target as a (rotating) harmonic

oscillator whose dipole moment is a function of internuclear separation

along the molecular axis. The oscillator motion is followed in a

coordinate system whose origin is fixed at the center-of-mass (CM) of the target molecule. The CM of the oscillator is at the center-of-mass of the dipole and the oscillator separation is much less than the ion-molecule separation. (This is consistent with the ideal dipole approximation.)

COLLISION MODEL AND INITIAL CONDITIONS

At high frequencies (i.e., on the order of molecular vibrations and fast rotations) the dipole moment of a polar molecule is not constant but a function of its internuclear separation. The separation of interest is usually that along a particular interatomic bond in the molecule.[9] The variation in dipole moment μ is assumed gaussian for these studies (i.e., $\mu = \mu_o e^{-a^2 x^2}$), where μ_o is the "static" dipole moment, a is the damping constant, and x is the reduced bond distance ($r - r_e$ where r is the instantaneous separation and r_e is the equilibrium bond separation). Such a variation is a reasonably representative approximation for diatomic and polyatomic molecules of interest.[9] To test the sensitivity of the results to the shape of the $\mu(x)$ variation, the damping coefficient a was selected so that $\mu = 2\mu_o/3$ at $x = \pm 0.05$ Å for oscillator set (A). The maximum x value for the free oscillator assigned was 0.05 Å (0.005 nm) in all cases. For oscillator set (B) $\mu = 0.02 \cdot \mu_o$ at $x = \pm 0.05$ Å. The latter approximation is probably more realistic for polar targets. The shapes of the two gaussian variations are shown in figure 1. The period of change in μ is $\tau_o \simeq 4\pi \sqrt{m_o/k_o}$, where k_o and m_o are the oscillator force constant and reduced mass. The values of k_o and m_o for the oscillator set the maximum values of $\dot{x}$ and x at infinite separation for fixed E_o. The m_o value is not the same as the mass of the target molecule. Its value was chosen so as to reduce computer time. The energy

values E_o chosen were 0.36 eV and 0.036 eV corresponding to stiff and soft (nearly thermal) oscillations. However, only 50 cases were studied for the former because computer time was prohibitive. A k_o value of 4.8×10^4 dynes cm^{-1} (0.48 Newtons/cm) was assigned for these calculations with an m_o value equal to ten times the mass of the hydrogen atom. This k_o value is one-tenth the ground state value for HCl. Integration for trajectories of all oscillators causes extended computer running times (minimum of 5 min. for $v = 5 \times 10^4$ cm sec^{-1}). This is because the oscillation period is only 10^{-2} of the characteristic rotational period τ_R where $\tau_R = 2 \sqrt{I/2E_R}$; E_R is the rotational energy and I is the moment of inertia. The oscillator motion somewhat separates out from the rotational and translational motion; however, it will be shown that the nature of the variation is important in determining the ion turning points. Individual collisions with stiff targets require as much as 10 minutes to one-half hour computer time which is clearly prohibitive if hundreds of cases must be studied.

Most of the collisions studied involved the soft oscillators with $E_o = 0.036$ eV. The total energy of the free oscillator is

$$E_o = \frac{1}{2} m_o \dot{x}^2 + \frac{1}{2} k_o x^2 \qquad (1)$$

where all quantities have been previously defined. The maximum displacement of the free oscillator at large distances from the ion is given by $(x_m)_o = \sqrt{2E_o/k_o}$, i.e., the separation where the oscillator energy is purely potential with no interaction. The initial separations x were chosen randomly in the interval $|x| < (x_m)_o$. Approximately 400 collisions have been studied for impact parameters B from 3 to 12 Å. These b

values correspond roughly to critical impact parameters for capture with CO and CH_3CN targets.[1-3] The oscillator energy is constrained to remain positive throughout interaction but is allowed to decrease in value. Such behavior is, of course, not possible for a quantum oscillator in the ground state which must have energy $\frac{1}{2}h\nu_o$. Thus the observed "cooling" of such oscillators applies only to molecules which are initially in excited vibrational states. It should also be noted that the classical oscillator approximation is least adequate in describing variations in energy of stiff oscillators since quantum gaps are relatively large. The differential equation of motion for the oscillator is

$$\ddot{x} = -2a^2(\mu e \cos \gamma/R^2 + k_o)x/m_o \qquad (2)$$

The first term is an interaction term whereas the second term is a conventional restoring force term for the oscillator. The relative magnitude of these terms is important in determining dipole behavior.

RESULTS

The probability of multiple reflection f_R for oscillating polar targets is composed with results for purely rotating polar targets f_R in table I. The results of set A are for an a^2 value which makes $\mu = 2\mu_o/3$ at $x = \pm.05$ Å. Results are presented for both CO and CH_3CN. Results for set (B) are for an a^2 value (1.6×10^3 Å^{-2}) which makes $\mu \approx 0.02\mu_o$ at $x = \pm.05$ Å and include only CH_3CN results. The effect of oscillations clearly depends on impact parameter, however, it is difficult to detect general trends in the results. The f_R value is uniformly higher than f_R for set (B) at several b values but drops to zero at b = 11 Å. The variation $\mu(x)$ for the oscillator is important;

this can be seen from the difference between identical random number sets

for different a^2 values at roughly the same b values.

Further, there is a dramatic effect on the capture cross section

as demonstrated by the plots of C_R vs. b^2 for CH_3CN in Fig. 2. There

are fewer points for the vibrating targets (a^2 for $\mu \approx 0.02\mu_0$ at

$x = \pm0.05 \overset{o}{A}$ and only 25 cases per point (compared to 50 cases) because of

the prohibitive computer running times. The results agree at low impact

parameters $b = 6$ and $8 \overset{o}{A}$. However, there are marked differences between

results for $b = 10 \overset{o}{A}$ as well as for $b = 11 \overset{o}{A}$. The differences between

C_R values are well outside the rough 10% variance in cross section be-

tween 25 and 50 case sets of trajectories. The oscillator studies were

not done for $b > 11 \overset{o}{A}$ since the C_R value approaches zero. The low-

ered C_R values are for "heated" oscillator collisions so the result is

meaningful for real molecules in the limits of the classical interaction

approximation. The effect of the oscillator on capture cross section will

be much less for CO than for CH_3CN since the polarizability term determines

the capture cross section for CO.[4-5]

The collision lifetimes are relatively insensitive to vibrations for

a given species and the average τ_R for multiple reflection collisions is

~2 to 3×10^{-11} sec for CH_3CN targets. It should be noted that the trajec-

tories were cut off at a maximum of 10 reflections so that no meaningful

maximum reflection time could be calculated. Results of previous studies

indicate that the average number of (multiple) reflections is 15 to 25 for

certain b values.[5]

Certain features of the energy exchange between the translational,

rotational, and vibrational degrees of freedom are shown in the plots of

Fig. 3. The modulation of the interaction due to the variation of μ with x is almost undetectable because the vibrational time scale is so small.

The modulation of the oscillator separation x via the ion-dipole interaction is evident in the region $R \sim 5$ $\overset{o}{A}$ as shown in fig. 4(a) for a CH_3CN target. The corresponding variation in oscillator energy is shown in fig. 4(b).

Multiple reflection behavior is shown in fig. 5(a) and for a representation collision. The hindered rotation accompanying multiple reflection is shown in fig. 5(b). The symmetrical nature of the net spiraling (due to multiple reflections) is somewhat distorted by the oscillator. However, the general features of this phenomenon are unchanged by the oscillator as is hindering of the dipole. The hindering of the CH_3CN target occurs at large ion-molecule separations ($\approx 7 - 8$ $\overset{o}{A}$) as can be seen from the decreasing envelope of the γ plot in fig. 5(b). The characteristic ion turning points of the ion-molecule complex are large, ~ 10 to 20 $\overset{o}{A}$ for CH_3CN.

COMPUTER MOTION PICTURES - "CLASSICAL TUNNELING"

Vibrational motion has been added to the ion-dipole movies which were described in refs. 5 and 10. The modulation of the oscillator which is suggested in the time history plots is confirmed in the movies. This modulation is of course dependent on the value of $\cos \gamma$, i.e., the ion-dipole orientation angle which depends on their relative motion.

In viewing the movies it was noted that there is a change in the mode of the oscillation in several instances. This change in mode occurs when the oscillator acceleration goes through zero; that is, when the restoring

force is balanced by the interaction term. This constraint of the oscilla-
tor so that it cannot relax to its equilibrium is somewhat analogous to
quantum mechanical tunneling through a potential barrier so we have chosen
to call it "classical tunneling". The time history plots of oscillator
coordinate x and velocity $\dot{x}$ in figure 6 show that $\ddot{x}$ stays near zero
for a significant fraction of an oscillation period (where $\dot{x}$ is nearly
constant).

CONCLUDING REMARKS

Preliminary studies of vibrational effects on multiple reflections,
collision lifetimes, and capture cross sections in ion-dipole collisions
have been completed. For thermal oscillators (E_o = 0.036 eV) the effect
of the vibrator depends on impact parameter as well as target species.
The fraction of multiple-reflection cases is a complicated function of
the oscillator model, particularly the shape of the dipole moment varia-
tion $\mu(x)$. The oscillator can have a dramatic effect on the capture
ratio C_R; this lowering of the capture cross section is particularly
sensitive to the damping constant a. The inclusion of additional degrees
of freedom, particularly if coupled, might markedly increase the collision
complex lifetimes. Vibrator studies must be extended to a variation in
parameters before more general conclusions can be drawn about the role of
the oscillator. "Classical tunnelling" of the oscillator via the ion-
dipole interaction suggests a mechanism for rearrangement and/or dissocia-
tion which operates without the force constant changing. Quantitative
conclusions regarding this and related phenomena require further study.

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TABLE I - MULTIPLE REFLECTION RESULTS FOR HARMONIC OSCILLATOR STUDY

FOR ION VELOCITY OF 5×10^4 CM SEC^{-1}, 25 COLLISIONS

STUDIED PER IMPACT PARAMETER

Polar molecule set (A)	Impact parameter, $\overset{\circ}{A}$ (10^{-10} nm)	Fraction of collisions with mult. ref. f_R (without oscillator)	Fraction of collisions with mult. ref. f'_R (with oscillator)
CO	3.0	0.24	0.16
CO	4.	.20	.16
CO	5.	.24	.16
CH_3CN	5.	.24	.20
CH_3CN	6.	.16	.08
CH_3CN	7.	.36	.48
CH_3CN	9.	.28	.36
CH_3CN	11.	.20	.20
set (B)			
CH_3CN	6.0	0.16	0.60
CH_3CN	8.	.24	.12
CH_3CN	10.	.24	.32
CH_3CN	11.	.20	.0

(A) $a^2 = 160\ \overset{\circ}{A}{}^{-2}$. (B) $a^2 = 1.6 \times 10^3\ \overset{\circ}{A}{}^{-2}$.
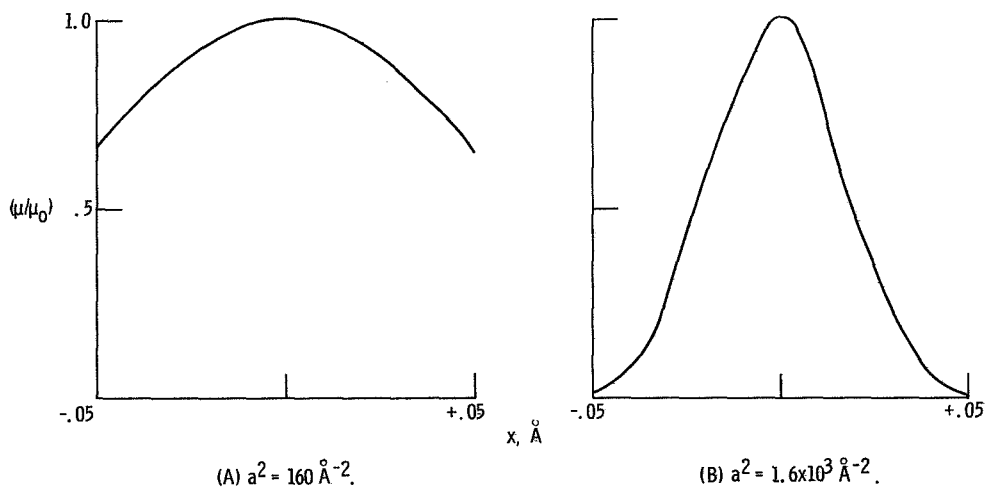
Figure 1. - Dipole moment variation for polar target oscillators studied (sets A and B), $|x_m|_0 = 0.05\ A$;
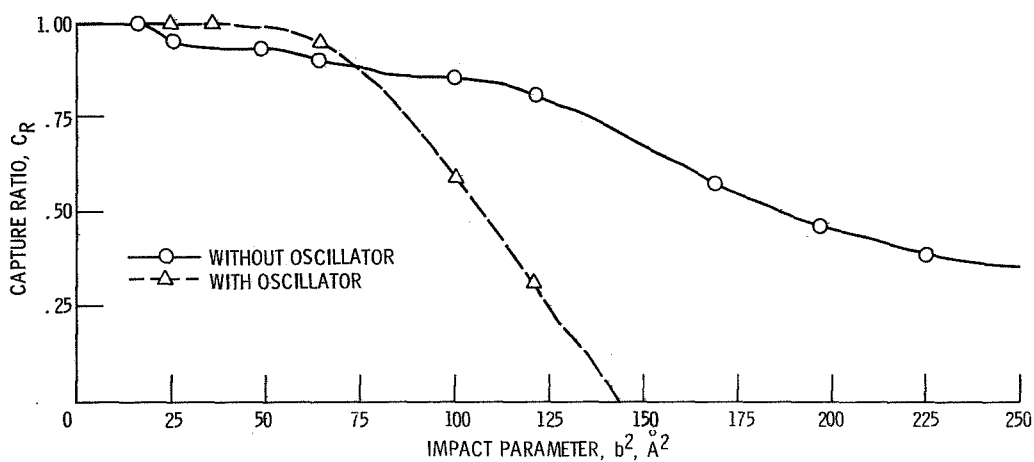
$$\mu = \mu_0 e^{-a^2 x^2}.$$

Figure 2. - Comparison of capture ratio variation with impact parameter for oscillating and pure rotating polar CH_3CN targets from set (B). Results are for an initial ion velocity of $5 \times 10^4\ cm\ sec^{-1}$ where the cross section

$$\sigma_c \equiv \pi \int_0^\infty C_R(b^2) d(b^2).$$

(A) OSCILLATOR SEPARATION.

(B) OSCILLATOR ENERGY.
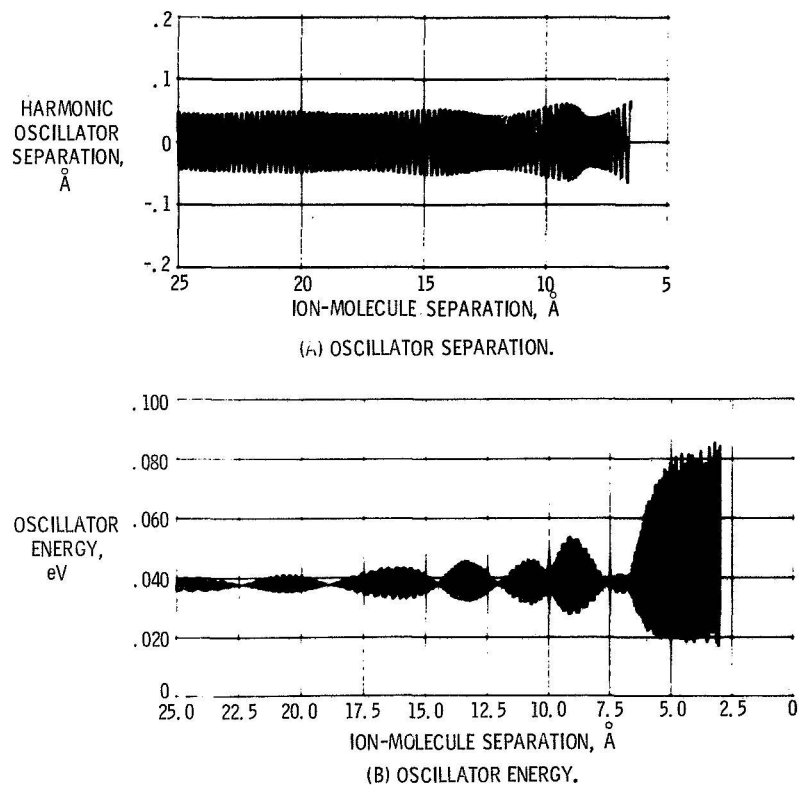
Figure 4. - Variations in oscillator separation and oscillator energy before reflection in a CH_3CN-parent ion capture collision with an oscillating target from set (B).

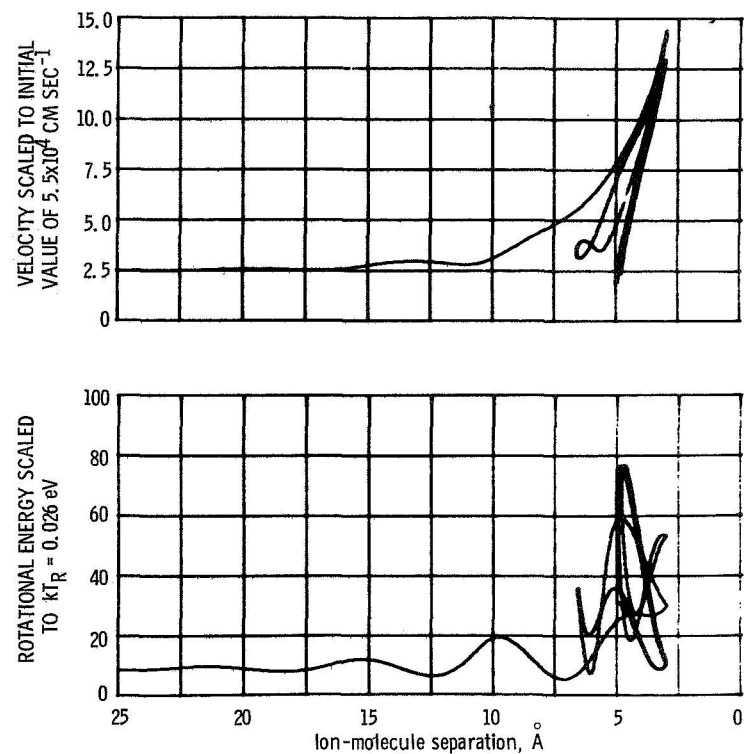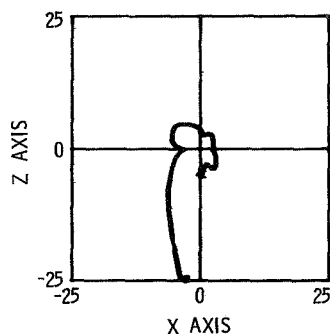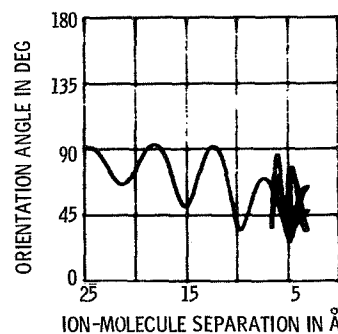
Figure 3. - Variation of ion velocity and polar molecule rotational energy during methyl cyanide-parent ion multiple reflection capture collision.

Z AXIS

X AXIS

(A) PROJECTIONS OF ION TRACE
IN CARTESIAN XY PLANE OF
CENTER-OF-MASS SYSTEM.

ORIENTATION ANGLE IN DEG

ION-MOLECULE SEPARATION IN Å

(B) ION-DIPOLE ORIENTATION ANGLE.

Figure 5. - Evidence for multiple reflection and hindered rotation behavior
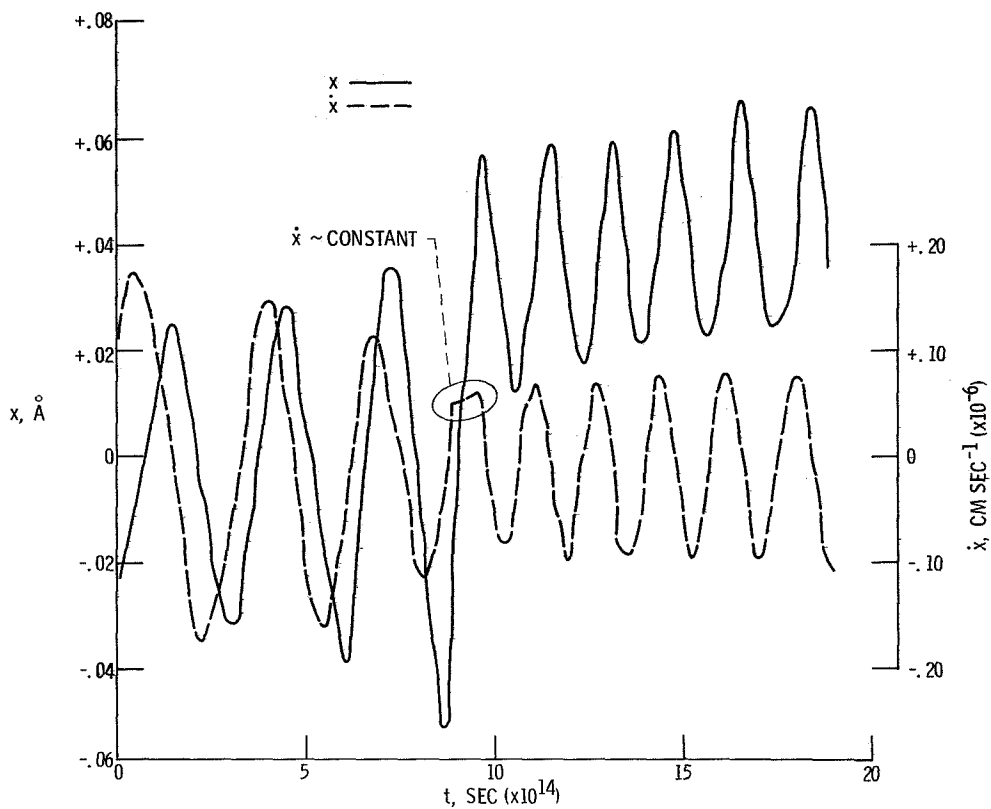in CH_3CN ion-dipole collisions with oscillating target.

Figure 6. - Variations of oscillator coordinates and velocity for ion-dipole collision demon-
strating "classical tunneling".